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## A thin inorganic composite separator for lithium-ion batteries

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## ABSTRACT

A thin inorganic composite membrane composed of 94 wt% Al<sub>2</sub>O<sub>3</sub> and 6 wt% styrene-butadiene rubber (SBR) polymer binder is prepared via an aqueous solution casting process. 1 wt% polyethylene glycol (PEG) is introduced into the casting suspension for the preparation of a 37 μm-thick inorganic composite separator. PEG plays a key role to enhance the stability of the casting suspension to separate the thin membrane from the substrate, and to increase the porosity of the membrane. The as-prepared Al<sub>2</sub>O<sub>3</sub>/SBR separator shows a superior thermal stability under 130 °C with no any shrinkage, higher electrolyte uptake/retention and ionic conductivity than the common polyethylene (PE) separator. In LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/graphite cells, the inorganic composite separator exhibits excellent cycling stability and good rate performance.

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## 1. Introduction

After successful applications in mobile electronic devices, lithium-ion batteries (LIBs) have been regarded as promising power sources for electric vehicles (EVs) and large-scale energy storage systems (ESSs) in recent years because of their advantages on energy density, power density and cycle lifetime [1–4]. In a typical LIB, an electrolyte-permeable porous separator is necessarily used to keep active electrodes (cathode and anode) apart but to permit the free flow of lithium ions through the liquid electrolyte filling in their open porous structure [5]. Even though the separator does not directly participate in the electrochemical reactions in a battery, it does significantly affect the cell performance of the battery as well as safety characteristics. Microporous membranes made from polyethylene (PE) and polypropylene (PP) matrices have widely used as separators for commercial lithium-ion batteries due to their good chemical stability and mechanical strength at room temperature. However, these organic separators usually have low melting points (135 °C for PE and 165 °C for PP) so that they could undergo obvious dimensional shrinkage even at the lower temperatures than their melting points, which may result in the direct contact of the anode and the cathode, i.e., short circuit. This internal short circuit may trigger thermal runaway of LIBs and

even a fire or explosion. Additionally, poor wettability of the polyolefin separators to nonaqueous electrolytes limits their high-power applications for EVs and ESSs [6,7].

Inorganic ceramic materials have been investigated as fillers into the polymer matrix to obtain the composite polymer separator with an enhanced thermal stability and electrolyte wettability [8–11]. In our previous papers [12,13], we prepared purely inorganic Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> porous membranes, which was used as separators in LiFePO<sub>4</sub>/graphite or LiMn<sub>2</sub>O<sub>4</sub>/Li cells and showed higher discharge capacity and rate capability, and better low-temperature performance than those using the commercial polymer separators due to their high porosity and wettability. In order to combine the advantages on the flexibility of composite polymer separators and the thermal stability of purely inorganic separators, inorganic composite separators containing inorganic ceramic powders as the main component are attractive [13–15]. The inorganic composite separators are composed of a high content of ceramic powders and a small amount of polymer binders or matrix. The former provides the separator with excellent thermal stability and electrolyte wettability, while the latter is designed for the flexibility of the separator. Recently, ceramic layers including SiO<sub>2</sub> [16], Al<sub>2</sub>O<sub>3</sub> [17,18], TiO<sub>2</sub> [19,20] were coated on commercial polyolefin separators in order to minimize the thermal shrinkage of polyolefin separators. This type of composite separators inherited the shutdown function of polyolefin separators, but also their high cost. Recently, Jung et al. [21] developed a ceramic separator composed of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> and 10–20% polymer binder on graphite negative electrode. Zhang et al. [14] blended CaCO<sub>3</sub> powers with Teflon emulsion (61.5% solid content in water) and hot-rolled the mixture into a self-standing membrane. However,

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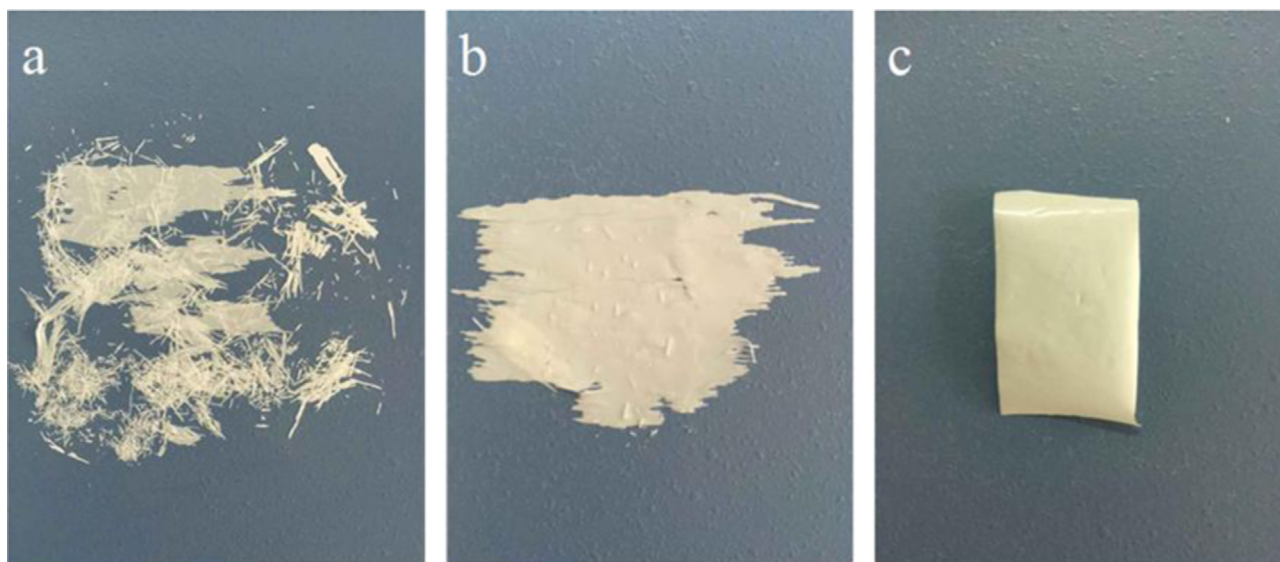


Fig. 1. Photographs of the membranes containing different contents of SBR. (a) 6%, (b) 20% and (c) 30%.

that inorganic composite separator had the thickness of 175–190  $\mu\text{m}$ , which was much thicker than commercial separators (25–40  $\mu\text{m}$ ). So far, it still keeps challenges to prepare a thin and self-standing inorganic composite separator. In order to achieve an inorganic composite separator with high porosity, the content of the polymer binder should be a low level, e.g. < 10%. Afterwards, the main difficulty is the poor mechanical strength of a thin composite separator with a small content of binder.

In this study, a thin and self-standing inorganic composite membrane composed of 94%  $\text{Al}_2\text{O}_3$  particles and 6% styrene-butadiene rubber (SBR) binder was prepared by a solution casting method. In order to obtain a 37  $\mu\text{m}$ -thick inorganic composite separator with the comparative thickness of commercial polyolefin separators, polyethylene glycol (PEG) was used as a multifunctional agent in the membrane-making process. Firstly, it was helpful to evenly mix  $\text{Al}_2\text{O}_3$  particles with the SBR binder. Secondly, it acted as a pore-forming agent for increasing the porosity of the separator. Finally, it was the key to separate the thin membrane from a glass substrate. During the membrane-making process, deionized water was used as the only solvent/dispersant, which made the preparation process environmental friendliness. Besides no thermal shrinkage, the thin inorganic composite separator exhibited attractive cell performance compared to the commercial PE separator in  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{graphite}$  cells. In the  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{graphite}$  cells, the  $\text{Al}_2\text{O}_3/\text{SBR}$  separator exhibits excellent compatibility with both the electrodes, long cycling stability and superior rate capability.

## 2. Experimental

### 2.1. Preparation of the composite separators

The inorganic composite separators were prepared by a solution casting method. Neutral activated alumina ( $\text{Al}_2\text{O}_3$ ) (300 mesh, Sinopharm Chemical Reagent Co., Ltd.) and  $\text{Al}_2\text{O}_3$  ultrathin particles (100–300 nm, Xianzheng Co., Ltd.) were mixed firstly by the mass ratio of 1:3. Then the mixed  $\text{Al}_2\text{O}_3$  particles and styrene-butadiene rubber (SBR, Jingbang Power Source Co., Ltd.) with polyethylene glycol (PEG, M.W.=2000, Sinopharm Chemical Reagent Co., Ltd.) were mixed thoroughly in deionized water to form a viscous slurry at room temperature. The mass of PEG is 1 wt% based on the total mass of  $\text{Al}_2\text{O}_3$  and SBR. Then the slurry was cast

on a clean glass substrate and spread by blade to obtain a membrane with a controllable thickness. After drying at 55  $^\circ\text{C}$  for 6 h, the glass substrate with the membrane was immersed in deionized water for 1 h to remove PEG. At the same time, the wet membrane was spontaneously separated from the substrate. After drying at 55  $^\circ\text{C}$  for 24 h, the as-prepared membrane was cut into discs ( $\Phi 16$  mm) for testing. For comparison, the no-PEG-assisted membranes with different ratios of  $\text{Al}_2\text{O}_3$  particles and SBR binder were prepared in a similar process with the addition and removal of PEG.

### 2.2. Physical and electrochemical measurements of the separators

The morphologies of the composite separators were investigated by a field emission scanning electron microscopy (FESEM, Hitachi S-4800). The thermal shrinkage of separators was observed after they were placed in an oven and heated at 130  $^\circ\text{C}$  for 40 min. The thermal stability of the separators was evaluated by differential scanning calorimetry (DSC, TA DSC 2920) in the temperature range of 50–200  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C min}^{-1}$  and thermogravimetric (TG) analysis (TGA 6000, Seiko Instruments) in  $\text{N}_2$  atmosphere from 100 to 800  $^\circ\text{C}$  at a heating rate of 20  $^\circ\text{C min}^{-1}$ . The contact angles between separators and the electrolyte of 1 M  $\text{LiPF}_6/\text{ethylene carbonate (EC)+dimethyl carbonate (DMC)}$  (1:1, w/w) were tested by the contact angle tester (DSA10-Mk2, KRUSS GmbH Germany). As described in our previous paper [12], the electrolyte uptake ( $U$ ) and retention ratio ( $R$ ) were calculated according to the following equations.

$$\text{Electrolyte uptake } U = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

$$\text{Electrolyte retention } R = \frac{W_x - W_0}{W_1 - W_0} \times 100\% \quad (2)$$

where  $W_0$  is the net weight of pristine separator,  $W_1$  and  $W_x$  are the initial and equilibrium weights of the wet separator after absorbing the electrolyte solution and standing at 50  $^\circ\text{C}$  for 30 min at least, respectively. For each testing point, three parallel measurements were carried out under the same conditions. For comparison, the electrolyte retention ( $R$ ) of some separator was normalized based on the 1st point of each measurement. All the

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